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ENGINEERING EXPERIMENT STATION
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October 26, 1961

Commanding Officer
Office of Ordnance Research, U. S. Army
Box CM, Duke Station
Durham, North Carolina

Attention: ORDOR-10

Subject: Progress Report No. 1, Project No. A-547
"Photochemically Induced Diels-Alder Reactions"
Covering the Period from January 2 to October 20, 1961
Grant No. DA-ORD-31-124-61-G-67

Gentlemen:

A report[1] has been made upon the yellow crystalline adduct derived from photochemical reaction between benzene and dimethyl acetylenedicarboxylate. This adduct was assigned the structure of dimethyl cyclooctatetraene-1,2-dicarboxylate; this assignment is now confirmed by comparison with an authentic sample of this (previously unreported) ester, kindly supplied by Dr. Arthur C. Cope. Vapor phase chromatography (v.p.c.) of the crude once-distilled adduct from benzene and dimethyl acetylenedicarboxylate gave the complex chromatogram summarized in Table I. While dimethyl cyclooctatetraene-1,2-dicarboxylate (retention time, 3.0 min.) is one of the chief products as expected, surprisingly another more prevalent product appears in 1.25 min. This run was peculiar, however, in that the crude product did not crystallize as usual; therefore the v.p.c. analysis needs to be repeated on the product of another run.

For comparison with the photochemical reaction of benzene, a preliminary run has been made upon reaction between thiophene and dimethyl acetylenedicarboxylate. Upon irradiation with ultraviolet light of 5 ml. of dimethyl acetylenedicarboxylate in 320 ml. of thiophene, there was obtained after removal of reactants 1.1 g. of crude residue. Distillation of this residue at about 50 microns pressure gave 0.14 g. (fract. No. 1) and 0.5 g. (fract. No. 2) of crude volatile product. Vapor phase chromatography gave the results shown in Table I. The most prevalent component in fraction No. 2 (retention time 1.95 min.) has the same retention time as dimethyl phthalate, which could

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[1] E. Grovenstein, Jr., and D. V. Rao, Tetrahedron Letters, No. 4, 148-150 (1961); 20 reprints of this report are attached.

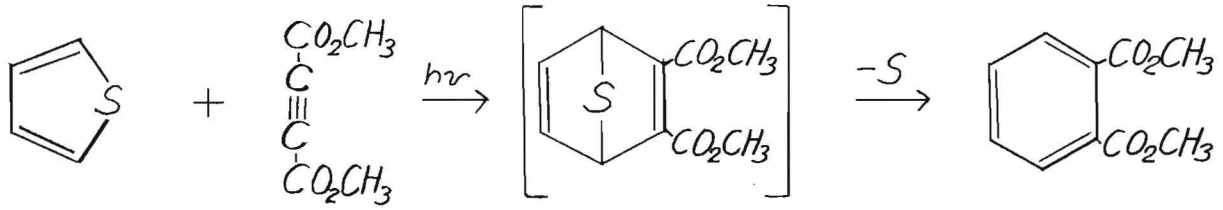
TABLE I

DATA FROM VAPOR PHASE CHROMATOGRAPHY OF PHOTOCHEMICAL ADDUCTS OF DIMETHYL ACETYLENEDICARBOXYLATE WITH AROMATICS+

Aromatic Reactant	Retention Times in Minutes with Relative Peak Heights in Parentheses for More Volatile Products other than Reactants
Benzene	1.25 (9.8); 1.85 (2.5); 2.35 (2.6); 3.0 (4.0); 3.6 (1.5); 4.85 (1.1); and traces at higher retention times
Thiophene	
Fract. No. 1	0.9 (1.5); 1.6 (19.7); 1.98 (4.5); 2.35 (1.8); 2.90 (0.8); 3.4 (0.4); 4.2 (0.4); 5.0 (0.3); 6.15 (0.8); 8.35 (0.5).
Fract No. 2	0.9 (1.6); 1.5 (0.7); 1.95 (11); 2.3 (2.2); 2.9 (1.1); 3.4 (0.7); 4.3 (0.3); 5.0 (0.3); 6.1 (0.2); 7.7 (0.4); 10.8 (0.2).
Naphthalene	1.3 (2.7); 1.75 (1.3); 2.0 (0.7); 2.4 (0.6); 2.8 (0.6); 3.6 (3.6); 4.9 (1.0); 6.9 (0.4); 8.5 (0.4); 9.8 (0.3); 13.4 (0.9).

+Run on Perkin-Elmer column O at 230° with helium as carrier gas.

conceivably be formed by the process:



The definitive identification of this component remains for future investigation.

A considerable effort has been devoted to study of the photochemical reaction of naphthalene with dimethyl acetylenedicarboxylate. Irradiation of a solution of naphthalene (20 g.) and 5 ml. dimethyl acetylenedicarboxylate in 310 ml. of acetone gave upon distillation in vacuo some 1.2 g. of volatile product. The vapor phase chromatogram of this product is shown in Table I. The major product has a retention time (3.6 min.) near that expected for a one-to-one adduct. Since our volatile reaction product has so far resisted attempts at purification by crystallization or simple distillation, a procedure has been devised for separation by preparative vapor phase chromatography. This procedure is now being applied to the product from a number of runs and it is hoped that sufficient quantitites of some of the fractions will soon be available to permit their identification.

The chromatograms summarized in Table I emphasize the complex nature of some of the reaction products obtained in the present work. In general we shall devote our major efforts to study of only the more prevalent products, that is, those which are underscored in Table I.

Mr. Paul G. Arapokos, who is a graduate student in the School of Chemistry, has served as research assistant during the period of the present report.

Respectfully submitted,

Erling Grovenstein, Jr.
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

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TETRAHEDRON LETTERS

No. 4, *pp.* 148-150

PHOTOCHEMICAL REACTION OF BENZENE WITH DIMETHYL ACETYLENEDICARBOXYLATE

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Tetrahedron Letters No. 4, pp. 148-150, 1961. Pergamon Press Ltd. Printed in the United States of America.

PHOTOCHEMICAL REACTION OF BENZENE WITH DIMETHYL ACETYLENEDICARBOXYLATE[1]

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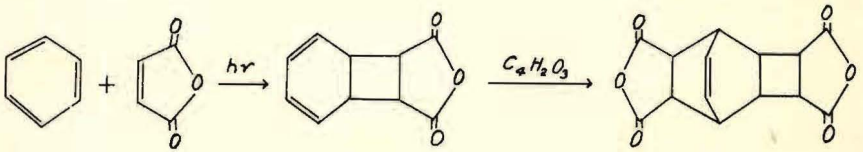
Atlanta, Georgia

(Received 8 February 1961)

The photochemical reaction of benzene with maleic anhydride has been shown to give an adduct of structure II[2,3]. This reaction evidently proceeds[1] by a photochemically activated 1,2-addition to give intermediate I followed by a 1,4-addition of maleic anhydride to give II. Similar photo-



I II

chemical reactions of maleic anhydride appear to occur with toluene, o-xylene, and chlorobenzene, especially in presence of a photosensitizer such as benzophenone[4]. We now wish to report a photochemical reaction of benzene with dimethyl acetylenedicarboxylate.

Irradiation at room temperature of a solution of dimethyl acetylenedicarboxylate (5.0 ml) in benzene (300 ml) with ultraviolet light for

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[1] This research was supported by the Office of Ordnance Research, U. S. Army.

[2] H. J. F. Angus and D. Bryce-Smith, Proc. Chem. Soc. 326 (1959); J. Chem. Soc. 4791 (1960).

[3] E. Grovenstein, Jr. and D. V. Rao, J. Amer. Chem. Soc. in press.

[4] G. O. Schenck and R. Steinmetz, Tetrahedron Letters No. 21, 1 (1960).

47 hours in a quartz apparatus previously described[5] gave, in addition to a difficulty volatile residue, 0.56 g of yellow crystals (m.p. 109.4-110.4°. Found: C, 65.39; H, 5.35; sapn. equiv., 107; mol. wt., 254. Calcd. for $C_{12}H_{12}O_4$: C, 65.43; H, 5.49; sapn. equiv., 110; mol. wt., 220). This methyl ester was purified by crystallization from methanol and sublimation at a bath temperature of 102° and a pressure of 0.03 mm. Saponification of the ester gave an acid which after recrystallization from water was isolated as yellow crystals of m.p. 206.5-208° (dec.) (Found: C, 62.34; H, 4.18. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20). The acid sublimed at a bath temperature of 190° and a pressure of 0.05 mm. The acid and the methyl ester readily decolorized a solution of potassium permanganate. The acid in acetic acid solution with a 5% Pt on carbon catalyst at room temperature and atmospheric pressure absorbed 3.0 moles of hydrogen per mole of acid in 4 hours and 0.6 additional moles in 91 hours. The acid in ethanol had ultraviolet absorption (shoulder) at 300 mμ (log ε = 2.84) and a maximum at 227 mμ (log ε = 4.20). The color of the acid and its ultraviolet absorption spectrum are similar to those reported for cyclo[8]tatetraenecarboxylic acid which has λ_{max}^{EtOH} 306 mμ (log ε = 2.92) and end-absorption at 220 mμ with log ε = 4.3. Also the infrared absorption spectra of the acid and its methyl ester are similar to those reported for cyclo[8]tatetraenecarboxylic acid and its methyl ester (note especially that the acid has C=C absorption at 6.14 μ while absorption at longer wavelength is expected for planar conjugated olefinic bonds or an aromatic ring). Moreover cyclo[8]tatetraenecarboxylic acid rather rapidly absorbs three molar equivalents of hydrogen and more slowly absorbs a fourth molar equivalent upon hydrogenation over a platinum

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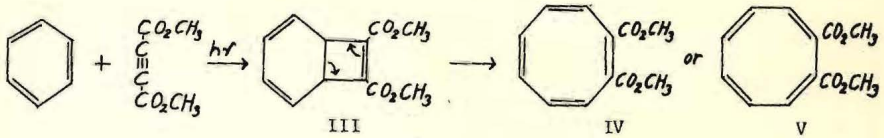
[5] E. Grovenstein, Jr. and S. P. Theophilon, J. Amer. Chem. Soc. 77, 3795 (1955).

catalyst in acetic acid solution[6].

The similarity in physical and chemical properties of the acid from reaction of benzene with dimethyl acetylenedicarboxylate with the known cycloöctatetraenecarboxylic acid and the lack of similarity with phenylmaleic and phenylfumaric acids strongly implies that the photochemical product has the structure IV and /or V of dimethyl cycloöctatetraene-1,2-dicarboxylate. A structure of this type can be formed by way of an intermediate III resembling that (II) proposed for the photochemical reaction of benzene with maleic anhydride. Intermediate III, however, undergoes isomerization to IV or V which is expected to be thermodynamically more stable than II and to be comparatively unreactive toward dimethyl acetylenedicarboxylate at room temperature[7].



III IV V

D. Bryce-Smith has kindly informed us that he has obtained 1 to 1 photo-adducts of acetylene derivatives with benzene etc. and that these appear to be derivatives of cycloöctatetraene. Moreover G. Büchi has considered a substituted cycloöctatetraene as one of several possible structures for a photo-adduct derived from benzonitrile and an acetylene derivative[9].

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[6] A. C. Copé, M. Burg and S. W. Fenton., ibid. 74, 173 (1952).

[7] Note that no appreciable amount of bicyclo[4.2.0]octa-2,4,7-triene appears to be in equilibrium with cycloöctatetraene. A temperature of 160-170° was used to effect reaction between cycloöctatetraene and diethyl acetylenedicarboxylate (W. Reppe, O. Schichting, K. Klager and T. Toepel, Ann. 560 1 (1948).

[8] D. Bryce-Smith, personal communication.

[9] G. Büchi, Seventh Reaction Mechanisms Conference, University of Chicago, Sept. 5, 1958.

FINAL REPORT

PROJECT NO. A-547

PHOTOCHEMICALLY INDUCED DIELS-ALDER REACTIONS

By

ERLING GROVENSTEIN, JR., and PAUL G. ARAPAKOS

GRANT NO. DA-ORD-31-124-61-G67
DEPARTMENT OF THE ARMY PROJECT NO. 59901004
ORDNANCE CORPS R & D PROJECT NO. TB2-0001
U.S. ARMY RESEARCH OFFICE (DURHAM) PROJECT NO. 2123-C

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COVERING THE PERIOD
JANUARY 2, 1961 to JANUARY 2, 1962

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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

FINAL REPORT

PROJECT NO. A-547

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COVERING THE PERIOD
JANUARY 2, 1961 to JANUARY 2, 1962

SUMMARY

A solution of dimethyl acetylenedicarboxylate in benzene when irradiated with ultraviolet light gives dimethyl cyclooctatetraene-1,2-dicarboxylate as the major volatile product. A preliminary account of this work has been published [Grovenstein and Rao, Tetrahedron Letters, No. 4, 148 (1961)].

Photochemical reactions of dimethyl acetylenedicarboxylate have been observed with naphthalene, thiophene, anisole, and chlorobenzene. The reaction products are in each case a more complex mixture than that obtained with benzene.

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DISCUSSION

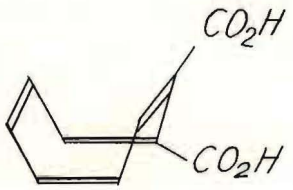
During the past year the photochemical reactions of dimethyl acetylenedicarboxylate with benzene, naphthalene, thiophene, anisole, and chlorobenzene have been under investigation.

The reaction of dimethyl acetylenedicarboxylate with benzene under activation by ultraviolet light was reported previously by us[1] to give a one to one adduct which was provisionally assigned the structure of dimethyl cyclooctatetraene-1,2-dicarboxylate. A published report of this work along with some additional work under the present contract has now appeared[2] and will not otherwise be covered in the present report. What remained to be done was to identify definitively the isolated crystalline dimethyl ester. Saponification[1,2] of the ester gave the corresponding dibasic acid. Proof that the two carboxyl groups of the acid were on adjacent carbon atoms was sought by dehydration to give a cyclic anhydride. However, the acid could be sublimed at a bath temperature of 173-210° at 0.05 mm. without appreciable change. Attempts to dehydrate the acid at 235-240° at 20-25 mm. pressure resulted in extensive decomposition and the small portion of the substance which distilled could not be appreciably redistilled at 0.05 mm. We conclude that our acid is unusually difficult to dehydrate for a cis-1,2-dicarboxylic acid and that the anhydride, if formed, was unstable under our reaction conditions and was transformed into higher molecular weight materials. This work does not disprove that our acid is cyclooctatetraene-1,2-dicarboxylic acid but suggests that the

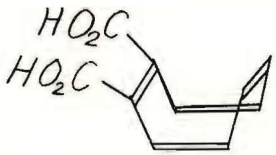
(1) E. Grovenstein, Jr., and D. V. Rao, Final Report Project No. A-421, Contract No. DA-01-009-ORD-709, Army Project No. DA-599-01-004, Ordnance R & D Project No. TB2-000, OOR Project No. 2123-C, Jan. 2, 1959 through Jan. 1, 1961, pp. 28-30.

(2) E. Grovenstein, Jr., and D. V. Rao, Tetrahedron Letters, No. 4, 148 (1961).

two carboxyl groups of the acid are not in the same plane. Such a non-planar arrangement is possible if the acid has the valence-bond structure I rather than II. The non-planar arrangement of the carboxyl groups in I might be



I



II

expected to be favored over the planar arrangement in II by analogy with fumaric and maleic acids.[3]

Attempts to prove the structure of our photochemical adduct of benzene and dimethyl acetylenedicarboxylate by partial hydrogenation of the corresponding acid followed by ozonization were underway when we received an authentic sample of the previously unknown (and never reported) dimethyl cyclooctatetraene-1,2-dicarboxylate.[4] Our ester was identical with the authentic sample on the basis of melting point, mixed melting point, infra-red and "mixed" infrared spectral comparisons.

The vapor phase chromatogram of the crude volatile product, which was distilled at 0.05 mm. at a temperature up to 150°, from photochemical reaction

(3) Dr. Arthur C. Cope in a personal communication has expressed a similar opinion concerning the structure of cyclooctatetraene-1,2-dicarboxylic acid and moreover has stated that definitive experiments to distinguish between the several possibilities are underway in his laboratory.

(4) The authentic sample was kindly supplied by Dr. Arthur C. Cope. Dr. Cope, in a personal communication, has stated that all of the isomeric cyclooctatetraenedicarboxylic acids have been prepared in his laboratory and thus there can be no doubt concerning the 1,2-arrangement of the carboxyl groups in our acid.

of benzene with dimethyl acetylenedicarboxylate, is shown in Table I. It is seen that the only major volatile product is dimethyl cyclooctatetraene-1,2-dicarboxylate which has a retention time of 2.95-3.05 minutes. Previously we had reported[5] another major peak of retention time of 1.25 minutes; however, repetition of this work gave only a minor peak here and we believe the peak is due to contamination of our vacuum line with naphthalene, with which we have been working extensively throughout much of the past year. The peak at retention time of 1.75-1.85 minutes may be due to biphenyl, which has about this retention time when run separately.

Irradiation of a solution of naphthalene and dimethyl acetylenedicarboxylate in acetone with ultraviolet light gives a considerable amount of product which can be distilled in vacuo. The vapor phase chromatogram of this product is shown in Table I and is of unusual complexity. The two chief products (according to peak areas) are of retention times of 3.7 and 13.4 minutes. A retention time of 3.7 minutes is intermediate between that of diethyl phthalate ($C_{12}H_{14}O_4$, retention time 2.9 minutes) and di-n-butyl phthalate ($C_{16}H_{22}O_4$, 8.4 minutes) and is suggestive of a molecular weight such as $C_{14}H_{12}O_4$, which could correspond to a dimethyl ester of a naphthalenedicarboxylic acid. While all identifications are still speculative it might be noted that a retention time of 1.3 minutes is close to that of beta-methylnaphthalene[6] (a weaker peak is also found at 1.5 minutes as expected for alpha-methylnaphthalene[6]); a peak at 1.75 minutes is as

(5) Progress Report No. 1 of this project, October 26, 1961.

(6) The methyl derivatives of naphthalene could result from methylation of naphthalene by methyl radicals from photodissociation of the acetone used as solvent here. For a discussion of the photodissociation of ketones in the vapor phase see, W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, Chem. Revs. 56, 49 (1956).

TABLE I

DATA FROM VAPOR PHASE CHROMATOGRAPHY OF PHOTOCHEMICAL ADDUCTS OF DIMETHYL ACETYLENEDICARBOXYLATE WITH AROMATIC COMPOUNDS

(Run on Perkin-Elmer column O at 230° with helium as carrier gas)

Aromatic Reactant	Retention Times in Minutes with Relative Peak Heights in Parentheses for More Volatile Products other than Reactants
Benzene	
Fract. No. 1	1.25 (1.0); 1.85 (2.9); 2.4 (0.5); 3.05 (16.9); 4.6 (0.3); 5.0 (0.3)
Fract. No. 2	1.15 (2.3); 1.75 (4.3); 2.3 (1.7); 2.95 (10.2); 4.5 (0.9); 5.0 (0.9); 6.0 (0.5)
Naphthalene	1.3 (2.7); 1.75 (1.3); 2.0 (0.7); 2.25 (0.6); 2.4 (0.6); 2.9 (0.6); 3.7 (3.6); 4.9 (1.0); 5.8 (0.4); 6.3 (0.3); 6.9 (0.4); 8.5 (0.4); 9.8 (0.3); 11.0 (0.2); 13.4 (0.9); 15.8 (0.2); 22 (0.07)
Thiophene	
Fract. No. 1	0.9 (1.5); 1.6 (19.7); 1.98 (4.5); 2.35 (1.8); 2.90 (0.8); 3.4 (0.4); 4.2 (0.4); 5.0 (0.3); 6.15 (0.8); 8.35 (0.5)
Fract. No. 2	0.9 (1.6); 1.5 (0.7); 1.95 (11); 2.3 (2.2); 2.9 (1.1); 3.4 (0.7); 4.3 (0.3); 5.0 (0.3); 6.1 (0.2); 7.7 (0.4); 10.8 (0.2)
Anisole	
Fract. No. 1	0.75 (10.4); 1.2 (2.6); 1.3 (2.4); 1.5 (2.4); 1.9 (9.9); 2.5 (2.5); 3.1 (4.0); 3.8 (13.2); 4.2 (3.5); 4.6 (3.0); 5.1 (6.1); 6.5 (1.3); 7.3 (1.0)
Fract. No. 2	0.7 (4.9); (bands 1.2-1.5 poorly resolved); 1.8 (3.4); 3.0 (1.1); 3.6 (2.7); 4.2 (1.3); 4.9 (1.5); 6.5 (0.5); 7.3 (0.4)
Chlorobenzene	
Fract. No. 1	0.8 (0.3); 0.95 (0.4); 1.75 (1.7); 2.4 (8.8); 3.0 (12.7); 3.25 (1.3); 3.7 (0.7); 4.3 (0.3); 4.8 (0.3); 5.1 (0.3); 5.8 (0.15); 6.7 (0.1)
Fract. No. 2	1.2 (4.4); 1.7 (3.6); 2.3 (12.3); 2.9 (17.9); 3.2 (7.3); 3.7 (5.3); 4.3 (2.7); 4.9 (4.1); 5.8 (1.6) 6.7 (1.2); 10.8 (0.7); 11.6 (0.7); 13.8 (0.5)

found for biphenyl; a peak at 2.0 minutes is as found for dimethyl phthalate; a peak at 2.9 minutes is as found for dimethyl cyclooctatetraene-1,2-dicarboxylate. Some progress has been made at separation of this complex mixture by preparative vapor phase chromatography and it is hoped that at least the major components can be resolved.

Preliminary experiments have been made upon photochemical reactions of solutions of dimethyl acetylenedicarboxylate in thiophene, anisole, and chlorobenzene. The vapor phase chromatograms of the distillable products of these runs are shown in Table I. Thiophene gave two major products of retention times near 1.6 and 2.0 minutes; the first of these corresponds to about what would be expected of a bithienyl (thiophene analog of biphenyl) and the second corresponds to the retention time of dimethyl phthalate (however, the dimethyl ester of a thiophenedicarboxylic acid would be expected to have about the same retention time). Anisole gave four major peaks at retention times of 0.75, 1.9, 3.8, and 5.1 minutes. The peak at 0.75 minute may correspond to a monomethyl derivative of anisole; the peak at 1.9 minutes could correspond to dimethyl phthalate; and the peak at 3.8 minutes could correspond to a methoxy derivative of dimethyl cyclooctatetraene-1,2-dicarboxylate. Chlorobenzene gave major peaks at retention times of 2.4 and 3.0 minutes. The peak at 2.4 minutes could correspond to a monochloro derivative of dimethyl phthalate or to a dichlorobiphenyl, while the peak at 3.0 minutes is in considerable doubt since a retention time of about 3.6 minutes would have been anticipated for a chloro derivative of dimethyl cyclooctatetraene-1,2-dicarboxylate.

Since appearance of our paper on the photochemical reaction between benzene and dimethyl acetylenedicarboxylate, a recent paper by Bryce-Smith

and Lodge[7] has stressed the generality of the photo-addition of acetylene to benzene to give cyclooctatetraenes. These workers report that methyl propiolate and benzene give methyl cyclooctatetraenecarboxylate, dimethyl acetylenedicarboxylate and benzene give a one to one adduct thought to be dimethyl cyclooctatetraene-1,2-dicarboxylate (cf. our work), phenylacetylene and benzene apparently give phenylcyclooctatetraene and traces of 1-phenylazulene, and acetylene and benzene give a complex mixture of products in which the presence of a trace of cyclooctatetraene is indicated.

(7) D. Bryce-Smith and J. E. Lodge, Proc. Chem. Soc., Sept., 333 (1961).

EXPERIMENTAL DETAILS

Irradiation of Dimethyl Acetylenedicarboxylate in Benzene.--Dimethyl acetylenedicarboxylate (5.0 ml., b.p. 96-97° at 20 mm.) was dissolved in 300 ml. of benzene and irradiated with ultraviolet light for 26 hours in a quartz apparatus previously described.[8] The benzene and unreacted dimethyl acetylenedicarboxylate was removed under vacuum with heat supplied as required by a steam bath. The residue was distilled in a modified Hickman still[9] and gave 1.21 g. of crude oily yellow crystals at a pressure of 0.10 to 0.03 mm. and a bath temperature of 95 to 151°. A dark-red glassy residue remained undistilled. The vapor phase chromatography of the crude yellow crystals from a similar run (but with 60 ml. of the benzene replaced by 80 ml. of acetone) are recorded in Table I; Fraction 1 is the main portion of the distillate and Fraction 2 is that portion which adhered to the condenser. The crude yellow crystals after washing with a little methanol gave 0.70 g. of crystals and after recrystallization from methanol and vacuum sublimation had m.p. 109.4-110.4°. On the basis of the data previously reported[1,2] this compound was tentatively assigned the structure of dimethyl cyclooctatetraene-1,2-dicarboxylate. This assignment is now fully confirmed by comparison of melting point, mixed melting point, infrared spectrum, and mixed infrared spectrum with a sample of the previously unknown dimethyl cyclooctatetraene-1,2-dicarboxylate, kindly supplied by Dr. Arthur C. Cope (see Footnote No. 4).

(8) E. Grovenstein, Jr., and S. P. Theophilou, J. Am. Chem. Soc. 77, 3795 (1955).

(9) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 66.

Sublimation of Cyclooctatetraene-1,2-dicarboxylic Acid.--This acid [m.p. 206.5-208° (dec.)] was prepared by hydrolysis of dimethyl cyclooctatetraene-1,2-dicarboxylate by the method previously described.[1,2] This acid could be sublimed at a bath temperature of 173-210° and a pressure of 0.05 mm. without appreciable decomposition. However, when the acid was heated at 20 to 25 mm. pressure at a bath temperature of 235-240° only a fraction of the acid sublimed. The yellow sublimate partially turned into a brown melt at 125-190° but was not completely molten up to 240°. Only a very small portion of the yellow sublimate could be resublimed at 0.05 mm. and 200°.

Partial Hydrogenation of Cyclooctatetraene-1,2-dicarboxylic Acid.--Cyclooctatetraene-1,2-dicarboxylic acid (3.26 g., 17.0 mmoles) was dissolved in 115 ml. of purified acetic acid containing 1 g. of prereduced 5% platinum on carbon catalyst. Upon vigorous agitation, the mixture absorbed by the end of 206 minutes 960 ml. (38.7 mmoles) of hydrogen at 743.8 mm. and 22.2°; absorption of hydrogen had nearly ceased at this point. Consequently, another gram of the platinum on carbon catalyst was added and the solution took up 426 ml. (17.2 mmoles) of additional hydrogen in 50 hours. Removal of the solvent in vacuo and recrystallization of the product from acetic acid gave 1.3 g. of product of m.p. 179-208°. After five sublimations, 0.57 g. of acid of m.p. 235-239° and 0.12 g. of m.p. 242-244° were obtained. The acid of m.p. 235-239° after recrystallization from acetone and two more vacuum sublimations had m.p. 256-257° and gave the following analysis which agreed with that calculated for a cyclooctadiene-1,2-dicarboxylic acid.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.165. Found: C, 61.24, 61.06; H, 6.26, 6.19.

Irradiation of Dimethyl Acetylenedicarboxylate and Naphthalene in Acetone

Procedure A.--Naphthalene (37 g.) was dissolved in 340 ml. of acetone, 20 ml. of dimethyl acetylenedicarboxylate was added, and the solution was irradiated in the usual quartz apparatus for 72 hours. The solvent was removed on a rotating evaporator under water-pump vacuum ultimately at steam bath temperature; finally some 25 g. of naphthalene was removed by distillation on the same apparatus but at 0.05 mm. pressure at 100°. The residue was dissolved in acetone, decolorizing charcoal added, and the solution heated and then filtered. The solution was concentrated to a minimum volume to give a homogeneous solution of about 30 ml. Addition of ether (some 200 ml.) brought about separation of a brown oily paste. The paste was separated from the ether solution by decantation. The paste upon working with a pestle in an open evaporating dish turned into an almost white powder as all of the ether evaporated. The powder had m.p. 120-190° and at 200° and higher evolved a gas. Resolution of the powder in a minimum quantity of acetone, treatment with charcoal, and reprecipitation with ether gave a powder of m.p. 175-185°. The ether solution from which the crude brown oily paste had separated was distilled finally in vacuo. At a bath temperature of 160-245° at 0.1 mm. in a modified Hickman still 2.5 g. of black to yellow liquid was obtained (some decomposition was apparently brought about by over-heating with an infra-red lamp during the distillation procedure). Upon redistillation under the same conditions an orange-yellow liquid was obtained.

Procedure B.--Naphthalene (20 g.) was dissolved in 340 ml. of acetone (which had been dried over Drierite and freshly distilled), 5.0 ml. of dimethyl acetylenedicarboxylate was added, and the solution was irradiated in the usual

quartz apparatus for 48 hours. The solvent was removed on a rotating evaporator at 25 mm. finally at steam bath temperature. Some 16 to 17 g. of naphthalene was recovered by distillation on the same apparatus at 0.05 mm. pressure and steam bath temperature. The residue was transferred to a modified Hickman still and distilled at 0.05 mm. at a bath temperature of 160-300°. An average yield of 2.1 g. of orange-yellow distillate was obtained in seven similar runs. In runs which were similar except that the quantity of dimethyl acetylenedicarboxylate was reduced to 2.0 ml., a yield of 1.0 g. of orange-yellow distillate was obtained with an irradiation time of 24 hours; increasing the irradiation time in this run to 42 hours did not appreciably alter the yield. The vapor phase chromatogram of the orange-yellow product is recorded in Table I.

Irradiation of Dimethyl Acetylenedicarboxylate in Thiophene.--A solution of dimethyl acetylenedicarboxylate (5.0 ml.) in thiophene (320 ml. freshly distilled at b.p. 84°) was irradiated in the usual quartz apparatus for 69 hours. After the first 24 hours of irradiation a transparent yellow solution was present in the cell, but at the end of 54 hours the solution had become dark brown and a dark brown film adhered to the inside walls of the irradiation cell. The solution was worked up in the same manner as described for naphthalene (Procedure B) and upon distillation Fraction 1 amounted to 0.14 g. and Fraction 2 to 0.50 g. See Table I for the vapor phase chromatogram of these fractions.

Irradiation of Dimethyl Acetylenedicarboxylate in Anisole.--A solution of dimethyl acetylenedicarboxylate (5.0 ml.) in anisole (320 ml. freshly distilled at b.p. 154°) was irradiated in the usual quartz apparatus for 101 hours. The reaction mixture was worked up in the usual manner as described for naphthalene (Procedure B) and upon distillation at a bath temperature of 145-240° at 0.04 mm.

gave 0.89 g. (Fraction 1) of amber colored liquid and a smaller portion of product which adhered to the condenser (Fraction 2). See Table I for the vapor chromatogram of these fractions.

Irradiation of Dimethyl Acetylenedicarboxylate in Chlorobenzene.--A solution of dimethyl acetylenedicarboxylate (6 ml.) in chlorobenzene (320 ml.) was irradiated in the usual apparatus for 48 hours. At the end of this time the solution was yellow in color and the inside walls of the irradiation cell were coated with a dark brown film. The reaction mixture was worked up in the manner described for naphthalene (Procedure B). The product upon distillation at a bath temperature of 105-180° at 0.04 mm. pressure amounted to 1.18 g. of mobile yellow liquid (Fraction 1) and a smaller portion of material which adhered to the condenser (Fraction 2). The vapor chromatograms of these fractions are recorded in Table I.

Respectfully submitted:

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